

The 9th Asia-Oceania Symposium on Fire Science and Technology

Material flammability: A combustion science perspective

James S. T'ien*, Makoto Endo

Department of Mechanical and Aerospace Engineering, Case Western Reserve University, Cleveland, Ohio, 44106, USA

Abstract

Extinction limits of solid fuels are examined in two flame configurations: stagnation-point diffusion flame and spreading flame. In the first part of the paper, using a combustion model for the stagnation-point flame, the existence of critical flame temperature and critical fuel mass flux for extinction are examined as a function of the flow parameter. In the second part of the paper, the importance of flame stabilization zone in spreading flames is illustrated by an experimental example. Understanding of the events occurring in this zone is crucial for addressing the question of solid extinction limits.

© 2013 International Association for Fire Safety Science. Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](#).
Selection and peer-review under responsibility of the Asian-Oceania Association of Fire Science and Technology

Keywords: Flammability limits of solids; Blow-off; Quenching; Critical extinction temperature; Critical fuel mass flux; Flame stabilization

1. Introduction

Material flammability is a very broad subject and may imply different aspects of material response to fire and ignition sources. This is manifested by the large number of material screening tests in existence: Limiting Oxygen Index (LOI), Lateral Ignition and Flame spread Test (LIFT), upward flame spread tests (UL-94V and NASA 6001 test 1 [1]), cone calorimeter, Steiner Tunnel test (ASME E84), just to name a few. The meanings and implications of these tests may be different and not necessarily simple and it will not be possible to discuss all of them here. In this paper we will concentrate only on one aspect of material flammability, namely the flammability or extinction limit of solid materials which will be examined from a fundamental science point of view.

Extinction as a basic flame phenomenon is an important research topic in combustion. Flammability limits of gaseous premixed flames have been studied extensively. For the non-premixed case (diffusion flames), the situation is more complicated and extinction limits can vary with test and flow configurations. In a diffusion flame, how and how fast the oxygen and fuel are brought together can have a profound effect on the limits. Furthermore if the fuel is initially in condensed forms (liquid or solid), a phase transformation is required before gaseous reaction can occur. The rate of supply of the fuel vapor to the gaseous reaction zone depends on the heat transfer from the flame resulting in a tightly coupled system. Generally a diffusion flame may consist of a number of regions; each may have a different function in sustaining and/or spreading the flame. In the following, a couple of example cases will be illustrated with a focus on the flame stabilization zone that controls the extinction limit of the flame. Note that solid fuels can be more complicated than liquid fuels since the pyrolysis processes are more complex with the possibility of producing char, tar and ash. Solids can also be composite in composition with different properties among its components.

* Corresponding author. Tel.: +1 216 368 4581; fax: +1 216 368 3007.
E-mail address: jst2@case.edu.

2. Flame stabilization zone

Figure 1 is a schematic of two spreading flames over solid samples. Spreading in concurrent flow is when the direction of flame spreading is the same as that of the main flow. An example is the upward spread in a buoyant environment or a downwind spread in a purely forced flow. Spreading in opposed flow is when the direction of flame spreading is opposite to that of the main flow. An example is the downward spread in a buoyant environment or an upwind spread in a purely forced flow. In both cases, the flame stabilization zone is located at the upstream edge of the flame where the fuel vapor first mixes with the incoming oxygen and combustion reaction is initiated. Assuming the incoming oxygen temperature is below the spontaneous temperature of the fuel, sustained reaction requires the Damköhler number be large enough in the flame stabilization zone [2]. Damköhler number is the ratio of flow time to reaction time. The size of the flame stabilization zone can be found by balancing the rate of upstream heat conduction to the air convective velocity. The resulting thermal-diffusional length is equal to α/U_∞ , where α is the gas-phase thermal diffusivity and U_∞ is the flow velocity near the stabilization zone. In a buoyant flame, U_∞ is of the order $(\alpha g)^{1/3}$ [3] and the length of the stabilization zone is $(\alpha^2/g)^{1/3}$. For typical values of α and normal gravity (g), this length is of the order of several millimeters. Despite the small size of the zone, it controls the flame extinction characteristics. Note that the flame standoff distance from the sample surface is smallest in the stabilization zones. Consequently, the fuel mass burning rate per area is the largest there and the gas-phase reaction rate and the heat release rate (per volume) are also the highest there. If reaction can be sustained in this zone, flame will exist and extend to downstream.

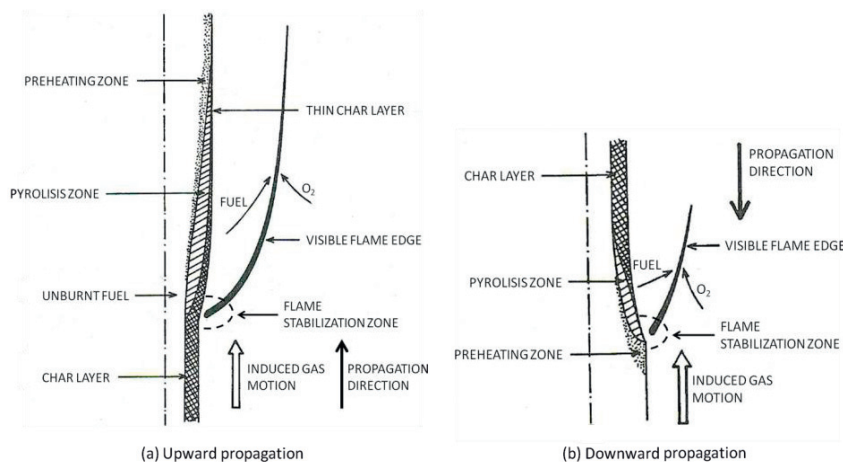


Fig. 1. Schematics on upward and downward spreading flames over a solid material (not drawn to scale).

Figure 1 shows that the relative positions of the stabilization zone with respect to other zones in the flame are different between the upward spread and the downward spread cases. From the point of view of the fresh solid fuel, it first sees preheating, then pyrolysis before reaching the stabilization zone for upstream spread (Fig. 1(a)). Although flame spread rate is largely determined by the pyrolysis and preheating regions, events in the small stabilization zone at the flame base control the flame existence and stability. In downward spread, preheating and stabilization are co-located with additional pyrolysis occurring downstream (Fig. 1(b)), therefore the stabilization zone also controls the spread rate in opposed spread [2]. Since solid properties can change during pyrolysis for complex fuels, the different order of pyrolysis and heating sequence between the two flame spreading modes can affect extinction behavior in unexpected ways. We will have further discussions on this in section 4.

3. Stagnation-point solid-fueled diffusion flame

The existence of several zones complicates the description of the spreading flames and it often becomes a distraction when the question of extinction limit is addressed. There is one diffusion flame configuration where only one zone exists. This is the stagnation-point flame as shown in Fig. 2. In this geometry, all the scalar quantities (temperature and species concentrations) are (quasi-) one-dimensional and the solid burning rate is uniform. Basically, the entire flame is the stabilization zone. Analysis of this one-dimensional problem is much simpler and key parameters affecting extinction can be sought out more readily. Mathematically, the governing system consists of ordinary differential equations, while for

spreading flames they are partial differential equations. We will first examine this simplified flame to see what can be learned before returning to the flame spreading case.

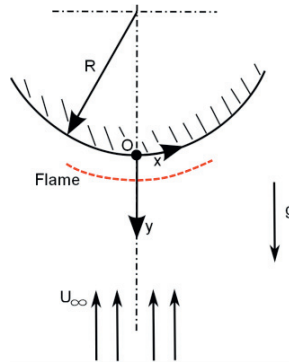


Fig. 2. Example of a diffusion flame near the forward stagnation point of a blunt-shaped solid fuel. Stretch (strain) rate: $a = 2U_\infty/R$ (forced flow, cylinder); $a = 3/2 U_\infty/R$ (forced flow, sphere); $a = (g/R)^{1/2}$ (buoyant flow)

3.1. Combustion model

The only fluid-mechanical parameter to describe the flow of oxygen in this configuration is the velocity gradient a near the stagnation region which has the unit of 1/time. In fluid mechanics, this is the flow straining rate and in the combustion literature this is also referred to as the flame stretch rate. There are a number of configurations to generate the same flame stretch rate: by an impinging an oxygen jet onto a solid plate (e.g. [4, 5]), by placing a blunt solid sample (spherical or cylindrical) in a oxygen flow in a wind tunnel (e.g. [6]) and utilizing bottom burning in a gravity field (e.g. [7, 8]). In the last case, the stretch rate is given by $a = (g/R)^{1/2}$, where g is gravity and R is the radius of curvature of the solid sample in the stagnation-point region. In a fixed gravity field, low stretch rate can be obtained with a solid of large radius of curvature.

In this configuration, computational analysis can be used readily as a tool to analyze the flame extinction behaviour. Using the combustion model on the burning of PMMA [9], several computed extinction boundaries will be presented and the near-limit flame properties examined. The model is formulated and solved non-dimensionally. A one-step finite rate combustion reaction is assumed with the non-dimensional reaction rate written as:

$$\varpi = Da Y_O Y_F \exp(-E/RT) \quad (1)$$

where E and T are the activation energy and temperature, respectively, Y_O and Y_F are the fuel and oxygen mass fractions respectively. Damköhler number Da is defined as

$$Da = B/a \quad (2)$$

where B is the pre-exponential factor of the reaction and a is the flow strain rate or the flame stretch rate. Both have the unit of one over time.

Heat loss from the flame was assumed from surface radiative loss only. The non-dimensional heat loss parameter S is given by:

$$S = (\sigma \varepsilon_s T_e^3 / \lambda_e) (\mu_e / \rho_e a)^{1/2} \quad (3)$$

where σ is the Stefan-Boltzmann constant, ε_s is the surface emissivity, λ , μ , ρ are gas conductivity, viscosity and density respectively. Subscript e denotes that the quantities are evaluated at free stream.

The solid mass burning rate \dot{m} (mass/area time) is given by

$$\dot{m} = (\rho_e \mu_e a)^{1/2} (-f_w) \quad (4)$$

where $-f_w$ is the non-dimensional burning rate to be calculated by the model.

Three sets of computed results will be presented. These include the variations of ambient oxygen mass fraction Y_{O_e} (environmental parameter), surface emissivity ε_s (heat loss parameter) and pre-exponential factor of chemical reaction B (chemical kinetics rate parameter).

3.2. Extinction limits as a function of flow parameter

Figure 3(a) shows the ambient oxygen limits (in terms of oxygen mass fraction in the oxygen/nitrogen atmosphere) vs. the flame stretch rate (or the flow strain rate). This is basically a re-plot of Fig. 2 in [9]. It shows that the extinction boundary is a strong function of the flow as represented by the flame stretch rate. The boundary consists of two branches: the existence of a high-stretch blow-off extinction boundary due to insufficient gas residence time (Da is too small in Eq. (2)) and a low-stretch quenching boundary due to excessive heat loss (S becomes too large in Eq. (3)). In both cases, the flame goes out because the non-dimensional reaction rate (ϖ in Eq. (1)) is reduced. In the blow-off case, ϖ is reduced as Da becomes too small; in the quenching case, ϖ is reduced because the flame temperature is lowered when S becomes too large. In other words, both extinction modes are affected by chemistry.

The two extinction branches merge when oxygen percentage is reduced. Near the merging point, both the flow residence time and the heat loss have comparable influence. Note that on the blow-off branch, the oxygen limit increases with the flame stretch rate but on the quenching branch, the opposite is true. Although Fig. 3(a) is plotted for a stagnation-point flame, the qualitative feature of the plot, *i.e.* the existence of low-residence-time blow-off extinction branch and a high-heat-loss quenching branch exists in diffusion flames of many configurations [10, 11]. In the spreading flame case, for example, a U-shaped boundary also was found if we replace the stretch rate a in Fig. 3(a) by the flow velocity [10]. One should, however, note that the scale in Fig. 3(a) is logarithmic for the stretch rate a . In other words, the range of quenching branch may be small. In this branch, the flame goes out as a weak low-intensity flame. Blow-off limiting flames are the opposite.

3.3. The question of critical flame temperature

Probably because of the complexity of solid materials and the un-availability of their combustion reaction kinetics, many fire researchers have proposed simplified criteria that can be input to fire calculations without the knowledge of chemistry. One of the proposed criteria is the critical (minimum) flame temperature [12–14]. In NIST Fire Dynamics Simulator's large eddy simulation code (fast kinetics) for example, a user supplied extinction criterion using a minimum flame temperature is included. The dependence of extinction temperature can be specified by the user. The default setting has the critical temperature varying with inversely with local oxygen percentage. Others have suggested the critical temperature may vary with fuels [14].

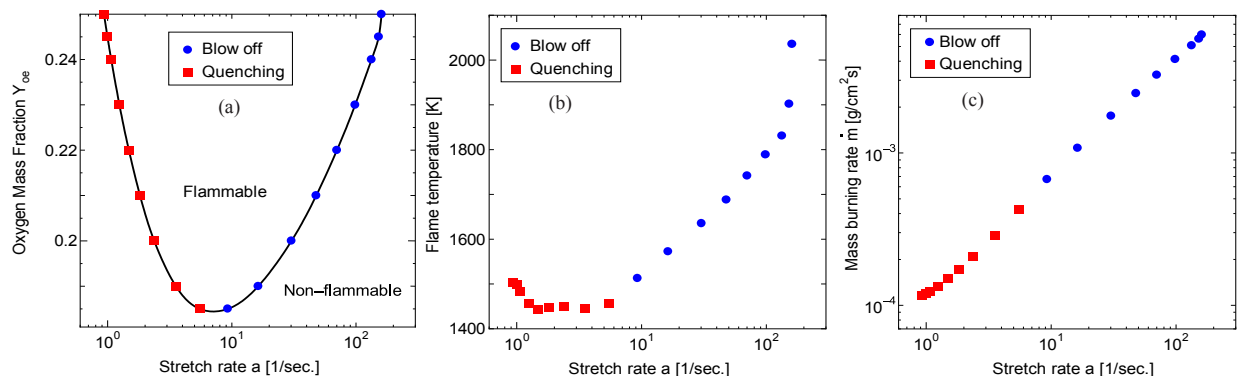


Fig. 3. Computed stagnation-point flame with ambient oxygen and flame stretch rate as variables ($\varepsilon_s=1$ and $B=5.047 \times 10^7 \text{ s}^{-1}$). a) extinction boundary; b) flame temperature along the extinction boundary; c) solid mass burning rate (mass flux) along the extinction boundary

Computed results on the flame temperature along the extinction boundaries in Fig. 3(a) are given in Fig. 3(b). Note that along the extinction boundary both the oxygen percentage and the stretch rate change. Fig. 3(b) shows the flame temperature along the blow-off boundary increasing monotonically with stretch rate (and oxygen percentage) monotonically. The extinction temperature can be very high at high stretch. The flame temperatures on the quenching branch are relatively low, varying between 1440 K and to 1510 K in this computation. Their relative insensitivity to stretch rate is due to the

shape of the quenching boundary in Fig. 3(a). As stretch rate is decreased, non-dimensional radiative heat loss increases but the limiting oxygen percentage also increases. These produce two opposing effects on flame temperature resulting in a nearly constant flame temperature along the quenching boundary. Note, however, the quenching branch is when stretch rate is less than 8 s^{-1} , a relative narrow range of slow flows.

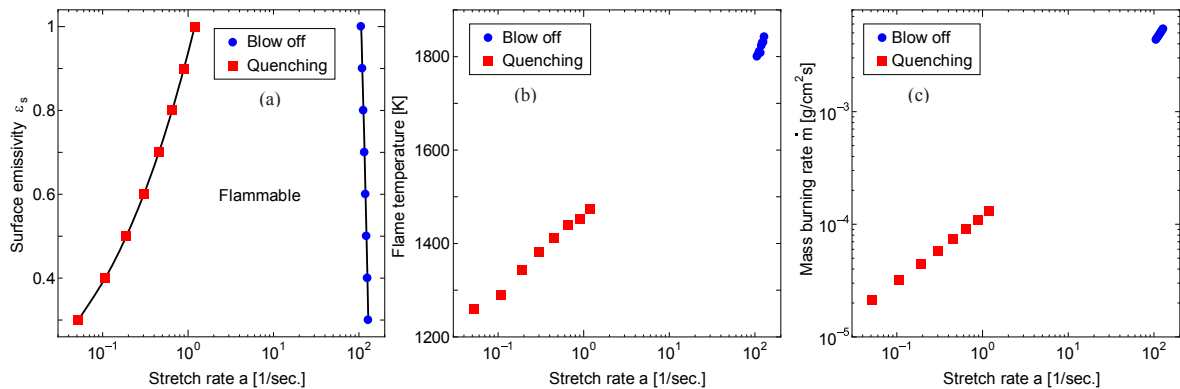


Fig. 4. Computed stagnation-point flame with surface emissivity and flame stretch rate as variables ($Y_{O_2}=0.2324$, air and $B=5.047 \times 10^7 \text{ s}^{-1}$). a) extinction boundary; b) Flame temperature along the extinction boundary; c) Solid mass burning rate (mass flux) along the extinction boundary

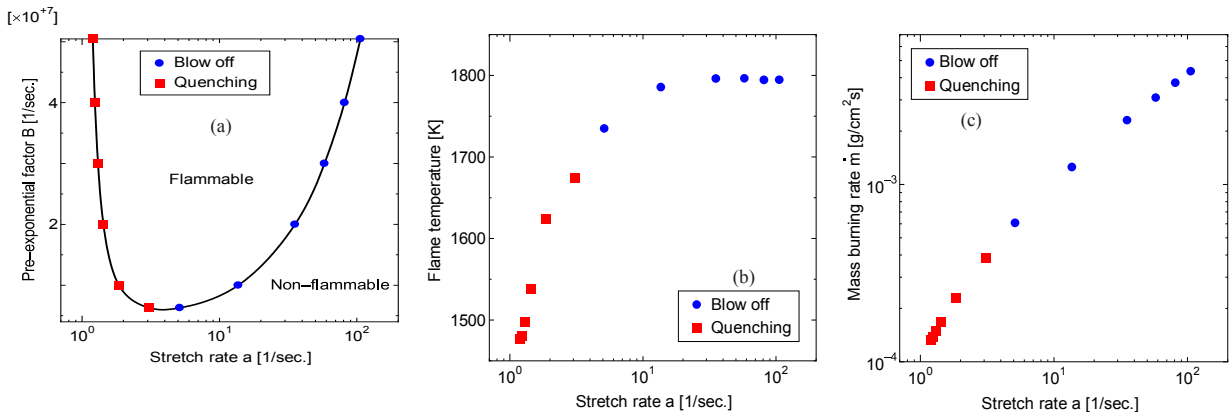


Fig. 5. Computed stagnation-point flame with combustion reaction pre-exponential factor and flame stretch rate as variables ($Y_{O_2}=0.2324$, air and $\varepsilon_s=1$). a) Extinction boundary; b) flame temperature along the extinction boundary; c) solid mass burning rate (mass flux) along the extinction boundary

To see whether a similar result occurs in other flame situations, Fig. 4(a) shows the extinction boundary at a fixed oxygen mass fraction (0.2324, air) but with a different heat loss parameter. The variation of the heat loss parameter is through the change of the surface emissivity ε_s , (see Eq. (3)). Fig. 4(a) again shows two extinction boundaries. The flammable range increases with the decrease of ε_s , as expected. On a percentage basis, the quenching branch has a higher sensitivity to ε_s , also as expected. Fig. 4(b) presents the corresponding flame temperature at the limits. In this case, the extinction temperatures vary monotonically with stretch rate over the entire range of stretch rate. If we look at the quenching branch only, higher heat loss has higher extinction temperature and occurs at higher stretch rate. The computed flame temperature for $\varepsilon_s = 0.3$ at $a = 0.53 \text{ s}^{-1}$ is only about 1260 K, a very low temperature. Clearly, in this simulated case, a constant extinction temperature does not exist.

A third computed case is given in Fig. 5. In this case, the chemical kinetic rate constant is varied through a change of the pre-exponential factor B , see Eq. (2). Fig. 5(a) shows the computed extinction boundary and the two branches that merge when B is sufficiently small. Fig. 5(b) gives the extinction flame temperature. The largest variation of flame temperature occurs along the quenching branch. Interestingly, the extinction temperatures level off at the high-stretch end of the blow-off branch.

So, what have we learned from this computational exercise? First, there is no unique critical extinction temperature for different materials. This is shown in Figs. 4 and 5 since they basically represent variations of material properties. The flame

temperatures at extinction are a strong function of flow parameters. For a given material but in different environments as represented by Fig. 3, there is a chance that a nearly constant extinction temperature may exist along the quenching branch. But the environmental parameter varied in Fig. 3 is through ambient oxygen percentage only. We have yet to test other environmental parameters such as pressure, inert gases in the oxygen stream or ambient and sample temperatures. In addition, as shown in Fig. 3(b), the range of stretch rates for the quenching branch is small. In a similar flammability boundary for spreading flame using oxygen percentage and flow velocity as coordinates, the dividing velocity between quenching and blow-off is found to be around 5 to 10 cm/s [10]. These stretch rate and flow velocity values are generally below the buoyant-induced ones in normal earth gravity. So to apply constant extinction flame temperature for fire on earth we need to be cautious.

In the literature, an extinction temperature of 1500 K (± 50 K) has been proposed for common hydrocarbons without flame retardants [13]. Quintiere chose 1573 K in his analysis [14]. We suspect that the experiments for deriving these values may not be in a low-enough stretch rate range for quenching extinction. Experimentally the measurement of the temperature for these weak low-stretch flames near the quenching limit is difficult. A special set-up is required if this is to be done on earth. Using a bottom porous gaseous burner with injected methane diluted with 40% nitrogen, Han et al [8] diagnosed the flame temperature at 1450 K at a buoyant stretch rate of 2 s^{-1} using non-intrusive Raman scattering. His experiment using a porous metal burner has conductive losses in addition to the radiative losses. In a model that includes detailed chemical kinetics and surface and flame radiation (narrow-band model) losses but without conductive loss, the computed extinction temperature is ~ 1300 K [8]. So the additional conductive loss can be the contributing factor for the difference between the measured and computed temperatures. Also using a bottom burning configuration for PMMA, Olson [7] measured a flame temperature of 1130 K for a sample with radius of curvature 75 cm (buoyant stretch rate $\sim 3 \text{ s}^{-1}$) using thermocouples without radiation correction. The peak temperature occurs on the oxygen side of the stagnation point. With low convective velocity near the flame, the radiation correction could be substantial, but the flame temperature should still be quite low. The extinction temperatures should vary with the reaction kinetic parameters as shown in Fig. 5(b). As an extreme example to show the variation of extinction temperature with chemical kinetics, a dry CO/ pure oxygen opposed-flow diffusion flame is solved using detailed kinetics and narrow-band radiation model [25]. Since the kinetics of dry CO is known to be very slow, at the predicted low-stretch rate limit (0.4 s^{-1}), the extinction temperature is 1850 K which is substantially higher than that for methane/air using the same computational scheme (~ 1300 K) [8].

3.4. The question of critical mass burning rate

Another simple flame extinction criterion proposed in the literature is a critical (minimum) mass burning rate of the solid fuel (mass flux, mass per area per time) (e.g. [15, 16]). A critical mass burning rate for extinction can be intuitively attractive since one way to put out fire is to reduce the fuel vapor supply to the gas-phase reaction zone. From the point of view of material modification, this can be achieved with char formation, intumescent layer or surface coolant. The first two provide heat and mass sinks as well as heat and mass transport resistance. But does a given solid have a critical magnitude at extinction for different extinction scenarios? Or put it differently, is the critical value a property of a given material?

Figures 3(c), 4(c) and 5(c) are the computed solid mass burning rate along the extinction boundary for the three cases examined previously. All of them show that the dimensional burning rates monotonically decrease with stretch rate. This can be seen from Eq. (4) which shows that the dimensional burning rate is dominated by the factor $a^{1/2}$. This dependence comes from the flame standoff distance from the solid surface which is proportional to $a^{-1/2}$. The present computation shows that the fuel mass flux at extinction is a strong function of the flow parameter. There is no constant limiting value even for a given fuel.

Experimentally, Olson [7] used a PMMA sample with a 75-cm radius of curvature in a bottom burning configuration (corresponding to a buoyant stretch rate of 3 s^{-1}) to reach the extinction limit for one-dimensional flame. The measured flame standoff distance from the fuel surface is 6.5 mm and the measured mass burning rate is $1.2 \times 10^{-4} \text{ g/cm}^2\text{s}$. This is close to the computed result in Fig. 3(c) but is an order of magnitude smaller than the reported value of $1.6 \times 10^{-3} \text{ g/cm}^2\text{s}$ for PMMA in [15] using a LOI type setup. This seems to verify that the limiting value is a strong function of flow or test setup. A related experiment is the measured PMMA mass flux to support ignition [17]. These authors found that the measured values at ignition decrease with pressure. So it is not a property of the material only. At lower pressure, the flame standoff distance is increased so a lower fuel supply rate is adequate to support the flame.

3.5. Other possible extinction criteria?

We can see from the above discussion that one of the major difficulties to have a simple extinction criterion is that diffusion flame behavior, including extinction, is affected by the flow. The flames near the high-velocity blow-off branch

have relatively high combustion intensities. The extinction is due to insufficient residence time to complete reaction in the stabilization zone. The flames near the low-velocity quenching branch have relatively low combustion intensities. The extinction is due to too high a heat loss compared with heat generation. The two extinction mechanisms manifest themselves in the different trends of flame property variations with flow parameters. On the other hand, we have seen that the extinction branches can merge as shown in Figs. 3(a) and Fig. 5(a). So with a modest variation of the flow magnitudes, a flame can switch from one branch to the other near the merging point. Present evidence shows that fire-related extinction can span across both branches. For example, upward and downward tests shown in Fig. 1 in normal gravity are likely to be blow-off extinction regime while the local extinction of a buoyant-convective flamelet (eddy of fuel vapor and oxygen) in a fire can be in the quenching regime.

One idea to form a unified criterion for extinction came from the theoretical model. The model consists of non-dimensional differential equations. Take the energy equation for example, it consists of a convective term, a conduction term, a heat release term by combustion reaction and possibly a gas radiation term. The non-dimensional chemical reaction term as expressed by Eq. (1) drops in magnitude when both the blow-off and the quenching limits are approached. The drops come from different parts within the expression of ϖ in Eq. (1). Blow-off occurs when Da in Eq. (1) becomes too small and quenching occurs when $\exp(-E/RT)$ in Eq. (1) becomes too small (temperature drops due to heat loss). As the products of the two, can the critical non-dimensional reaction rate ϖ be the same at both limits and be a constant along the extinction boundary? This idea has been proposed in [18, 19]. Because of the sensitivity of chemical reaction to temperature and the fact that at the limits the temperature drop is very steep, a computational procedure different from that used in [9] will be needed to obtain the accuracy necessary to answer this question. Future work is needed.

4. Need for testing in spreading flame configurations

The one-dimensional stagnation flame burner allows simple characterization of extinction both experimentally and theoretically. It is probably the most used configuration in combustion research for gaseous combustion. Although it has been used in solid combustion, its application to charring solid is limited. This is because the stagnation burner works best if the flame is stationary and the combustion processes are steady. Many commercial solid materials produce char and ash so that the burning characteristic at a fixed location is not steady. With the formation and accumulation of char and/or ash near the surface, the evolution of fuel vapor is impeded and the initial flame becomes weakened which may become extinct with time. In a large solid sample, however, the locally ignited flame may spread to a new location looking for fresh fuel that is not covered with a char layer. So, multi-dimensional test configurations allowing the flame to spread such as the UL-94 tests are needed for these fuels. The difference between flame spreading in concurrent flow (e.g. upward) and in opposed flow (e.g. downward), however, can complicate the test results as will be demonstrated by the experimental findings given below.

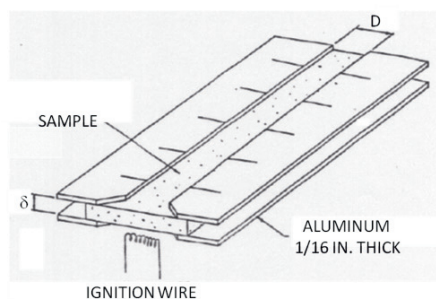


Fig. 6. Schematic of sample holder for testing upward and downward spread limits of rigid polyurethane foam slab [20].

Using rigid polyurethane foam as the sample, tests were carried out in an environmental chamber where oxygen percentage was varied [20]. The sample and mounting method is shown in Fig. 6. Depending on which end of the sample the ignition source is applied, the upward and downward flame spread oxygen limits are determined. Flame that did not propagate all the way to the end of the sample (length is 14 in or 35.54 cm) is regarded as extinction. Fig. 7 shows the photos of two samples where the flame goes out midway along the sample length. The spreading front of the downward case (the flame base) shows a sharp pyrolysis front marked by the charred surface. By contrast, the spreading front for the upward case (the flame tip) has a gradually darkened area but with a blackened flame base. These two samples near the extinction limits give a first indication of the difference between extinction limits of the two orientations. Fig. 8 shows the

upward and downward flame spread oxygen limits as a function of sample thickness. The downward oxygen limits are nearly independent of sample thickness. The upward limits have a strong dependence which increases with sample thickness. There are two upward limits shown. One with higher oxygen percentage above which the flame propagates over the entire sample consuming all the solid fuel in-depth except a char layer at the surface. A cut-away sample after the test is shown in Fig. 9(b). There is another upward limit at lower oxygen percentages. The flame also propagates all the way along the sample length but only consumes a portion of the top layer of the solid fuel. This is shown in Figs. 9(a). What is more surprising is that upward spread has a higher oxygen limits than those for the downward spread. In other word, there is a region where flame will spread downward but not upward. This is contrary to our experience with most materials. Our explanation has to do with char formation and how it affects the event at the flame stabilization zone.

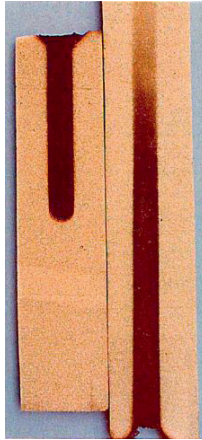


Fig. 7. Front photos of charred rigid polyurethane samples with flames stopped in the middle of the samples. Left: downward spread. Right: upward spread. [20]

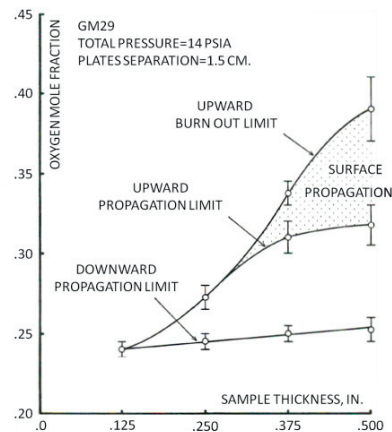
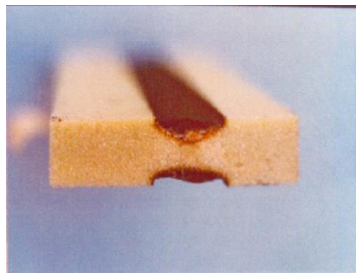
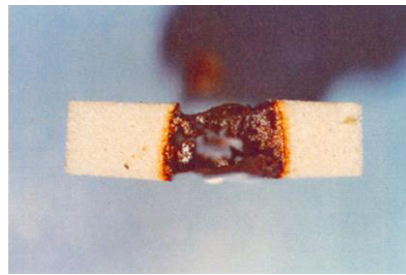


Fig. 8. Flammability map of a slab of rigid polyurethane foam (1.5-cm width), GM-29 [20].



(a) Surface propagation at Oxygen mole fraction=0.36



(b) Sample burnout at Oxygen mole fraction=0.44

Fig. 9. Cut-away cross section of rigid polyurethane samples at two oxygen environment. Flame spread all the way over the sample surface. [20]

Note that while the heat feedback from the flame is the strongest at the flame base due to the smallest flame standoff distance, for the upward spreading flame, the solid fuel located there is at the end of its pyrolysis processes (see Fig. 1(a)). The composition of the pyrolyzed gases, their evolving rates to the gas phase will depend on the entire heating history of the solid under the flame. For a non-charring fuel, the solid temperature in the stabilization zone has already been heated up through the pyrolysis region. This explains why the upward spread limit is wider than that for the downward case for those fuels. However, with char formation occurring during the entire pyrolysis period (zone), the flame also sees a char-covered solid in the stabilization zone. The reduced mass flux from the char layer overwhelms the heating effect to make the upward configuration less flammable. The thickness dependence of the spreading limit in Fig. 7 is due to the amount of fresh fuel that is available to build up a char layer. For foam samples, thin specimen has less material to form char.

In downward spread, the pyrolyzed gases in the flame stabilization zone are the first ones emerging from the material. As illustrated in Fig. 1(b) and observed in the experiment, char begins to form at slightly downstream of the flame anchor point. The stabilization zone in downward spread is essentially free of char-coverage hence a stronger flame at the stabilization zone. This explains the reversal of oxygen limits between the upward and downward spreads. Char may shorten the size of the downstream flame since it reduces the pyrolysis rate in the downstream zone. But, this has smaller influence on the extinction limit of downward spread.

We use this particular example to show the complexity and the subtlety of the material extinction question and the necessity to consider the event occurring in this small flame stabilization zone. Very often we are overwhelmed by the size of the entire flame, but this small flame anchoring zone is critical when we want to address the question of extinction limit of materials. The different time sequence of the flame stabilization zone relative to other pyrolysis events also can have implications to the interpretation of cone calorimeter measurement to be discussed next.

5. A remark on cone calorimeter measurement

Cone calorimeters have been a popular device for material flammability testing in recent years (*e.g.* [21-24]). By applying a specified radiant flux to the sample, the response of the material can be measured. This results in simpler test procedures and the use of smaller size samples. The applied heat flux essentially decouples the flame dynamics where a two-way interaction exists: the flame provides the heat flux to the solid and the solid feedbacks the fuel vapor to the flame. The question with the cone measurement is how to interpret the material response as related to the flame behavior especially regarding to the extinction limit.

One of the interesting quantities measured by the cone is the time history of the heat release rate. Heat release rate is directly related to mass pyrolysis rate of the material. The peak of heat release rate (PHRR) has been found either early or late in the heating process. Sometimes more than one peak has been recorded. For extinction consideration, the PHRR seems important. To sustain a flame, the PHRR should occur at the flame stabilization zone. As discussed earlier, this can occur early in the heating process in downward (opposed-flow) spread and late in the heating process in upward (concurrent-flow) spread. Also, as we demonstrated that limiting material burning rates can be a strong function of flow conditions. To relate the heat release rate response to flame behavior, especially regarding the extinction characteristics, with a science-based flame theory would be very desirable. Currently, most studies are through rating correlations. We note that correlation of flame spread results using UL-94 and cone-calorimeter measurement has not been perfect [21].

6. Concluding remarks

From the fundamental point of view, flame extinction is a phenomenon of nonlinear interaction between chemical kinetics and transport processes. For solid materials the kinetics and transport include those occurring in the condensed phase. The lack of detailed knowledge and adequate data in the solid phase has prevented a quantitative prediction from first principles. However, even simplified models based on combustion theories can help clarify the question of solid extinction phenomena.

In this paper, we used two flame configurations to examine the solid extinction phenomena. In the stagnation-point burning case, we use a theoretical model to evaluate two proposed criteria for extinction: a critical flame temperature and a critical fuel mass flux (burning rate). We found that almost in all cases, these quantities are a function of the flow parameter. In the quenching regime, there is a hope that the extinction flame temperature can be approximated as a constant for a given fuel. But, it is also pointed out the quenching flow regime is limited and many of the flammability tests are in the blow-off regime. The experimental example of the spreading flames is to illustrate the importance of the flame stabilization zone - a zone which is small in size but is critical in determining flame extinction limits. In a charring solid, the interaction of this zone with the rest of flame can yield interesting and un-expected results such as the limit reversal between upward and downward spreads.

Acknowledgement

The supports by NASA and Underwriters Laboratories are greatly appreciated. We also like to thank Professor Naian Liu and Mr. Michael Johnston for their comments on the manuscript.

References

- [1] Flammability, Offgassing, and Compatibility Requirements and Test Procedures, NASA-STD-6001A, 2008.
- [2] Frey, A. E., T'ien, J. S., 1979. A Theory of Flame Spread Over a Solid Fuel Including Finite Rate Chemical Kinetics, *Combustion and Flame* 36, p. 263.
- [3] Jiang, C.-B., T'ien, J. S., Shih, H.-Y., 1996. Model Calculation of Steady Upward Flame Spread over a Thin Solid in Reduced Gravity, *Proceedings of the Combustion Institute* 26, p1353.
- [4] Holve, D. J., Sawyer, R. F., 1975. Diffusion Controlled Combustion of Polymers, *Proceedings of the Combustion Institute* 15, p. 351.
- [5] T'ien, J. S., Singhal, S., Harold, D. P., Prahl, J. M., 1978. Combustion and Extinction in the Stagnation-Point of a Condensed Fuel, *Combustion and Flame* 33, p.55.
- [6] Tsuji, H., Yamaoka, I., 1967. The Counterflow Diffusion Flame in the Forward Stagnation Region of a Porous Cylinder, *Proceedings of the Combustion Institute* 11, p. 979.
- [7] Olson, S. L., T'ien, J. S., 2000. Buoyant Low-Stretch Diffusion Flames Beneath Cylindrical PMMA Samples, *Combustion and Flame* 121, p.439.
- [8] Han, B., Ibarreta, A. F., Sung, C. J., T'ien, J. S., 2005. Experimental Low Stretch Gaseous Diffusion Flames in Buoyancy-Induced Flow Fields, *Proceedings of the Combustion Institute* 30, p. 527.
- [9] T'ien, J. S., 1986. Diffusion Flame Extinction at Small Stretch Rate: The Mechanisms of Radiative Loss, *Combustion and Flame* 65, No.1, p. 31.
- [10] Ferkul, P. V., T'ien, J. S., 1994. Model of Low-Speed Concurrent Flow Flame Spread over a Thin Fuel, *Combustion Science and Technology* 99, p. 345.
- [11] Chao, B. H., Law, C. K., T'ien, J. S., 1990. Structure and Extinction of Diffusion Flames with Flame Radiation, *Proceedings of the Combustion Institute* 23, p. 523.
- [12] Macek, A., 1976. Flammability Limits: Thermodynamics and Kinetics, *American Society of Mechanical Engineers* 76, p. 1076. National Bureau of Standards, Gaithersburg, MD.
- [13] Williams, F. A., 1981. A Review of Flame Extinction, *Fire Safety Journal* 3, p. 163.
- [14] Quintiere, J. G., Rangwala, A. S., 2004. A Theory for Extinction Based on Flame Temperature, *Fire and Materials* 28, p. 387.
- [15] Zhubanov, T. B., Gibov, K. M., 1988. Oxygen Index and Minimum Limiting Rates of Polymer Combustion, *Fire and Materials* 12, p. 169.
- [16] Quintiere, J. G., 2006. A Theoretical Basis for Flammability Properties, *Fire and materials* 30, p. 175.
- [17] Fereres, S., Lautenberger, C., Fernandez-Pello, C., Urban, D., Ruff, G., 2011. Mass Flux at Ignition in Reduced Pressure Environments, *Combustion and Flame* 158, p.1301.
- [18] Narayanan, P and Trouve, A., 2009. "Radiation-driven Flame Weakening Effects in Sooting Turbulent Diffusion Flames," *Proceedings of the Combustion Institute* 32, p. 1481.
- [19] T'ien, J. S., 2011. Presentation at FM Global Fire Modeling Workshop, May 22-25.
- [20] Maradey, J. F., T'ien, J. S., Prahl, J. M., 1977. "The Upward and Downward Flame Propagation Limits of Rigid Polyurethane Foams," CWRU Report, FTAS/TR-77-131.
- [21] Morgan, A. B., Bundy, M., 2007. Cone Calorimeter Analysis of UI-94 V-Rated Plastics, *Fire and Materials* 31, p. 257.
- [22] Hees, P., Andersson, P., Hjolman, M., Wenne, N., Hassan, M. A., 2010. Use of the Cone Calorimeter and Cone Tools Software for Development of Innovative Intumescent Graphite Systems, *Fire and Materials* 34, p. 367.
- [23] Cogen, J. M., Lin, T. S. and Lyon, R.E., 2009. Correlations Between Pyrolysis Combustion Flow Calorimetry and Conventional Tests with Halogen-Free Flame Retardant Polyolefin Compounds, *Fire and Materials* 33, p. 33.
- [24] Scharfel, B., Hull, T. R., 2007. Development of Fire-Retarded Materials-Interpretation of Cone Calorimeter Data, *Fire and Materials* 31, p. 327.
- [25] Frate, F. C., Bedir H., Sung, C. J., T'ien, J. S., 2000. On Flammability Limits of Dry CO/O₂ Opposed-Jet Diffusion Flames, *Proceedings of the Combustion Institute* 28, p. 2047.